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A VARIATIONAL FORMULATION FOR COUPLED PHYSICOCHEMICAL FLOWS DURING FINITE DEFORMATIONS OF CHARGED POROUS MEDIA

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Abstract—Polymer gels, hydrated biological tissues and other charged porous media may exhibit macroscopic coupling between solid deformations and internal fluid, chemical and electrical flows. In this manuscript, we develop a variationally motivated finite deformation theory for describing such coupled phenomena. The formulation combines mathematical descriptions of the power balance associated with solid deformation and fluid and solute flows for an arbitrary number of solute species, and includes the macroscopic phenomenological coupling relations of nonequilibrium thermodynamics. Particular implementations of the theory are discussed for a charged, porous medium interacting with a binary electrolyte and for the addition of a third, possibly charged solute species to such a system. This theoretical framework is suitable for modeling physicochemical interactions in a large class of hydrated porous media.

1. INTRODUCTION

Polymer gels and hydrated biological tissues (e.g., articular cartilage, intervertebral disk, meniscus, blood vessels, etc.) are often modeled mechanically as saturated porous media. In such continuum formulations, microstructural fluid–solid interactions are represented by macroscopic coupling between tissue deformation, fluid pressure and fluid flow. Although this approach adequately represents tissue behavior over a wide range of physical situations, other microstructural interactions of electrical or chemical origin may produce additional macroscopic behaviors beyond the scope of such theories. For example, the purely mechanical approach is not sufficient for problems involving electrokinetic transduction, osmotically induced swelling or nutrient transport.

As an example of a biological material that exhibits such macroscopic coupling phenomena, we consider articular cartilage. The solid matrix of this tissue, which occupies approximately 20% of the total tissue volume, is composed of a complex assemblage of

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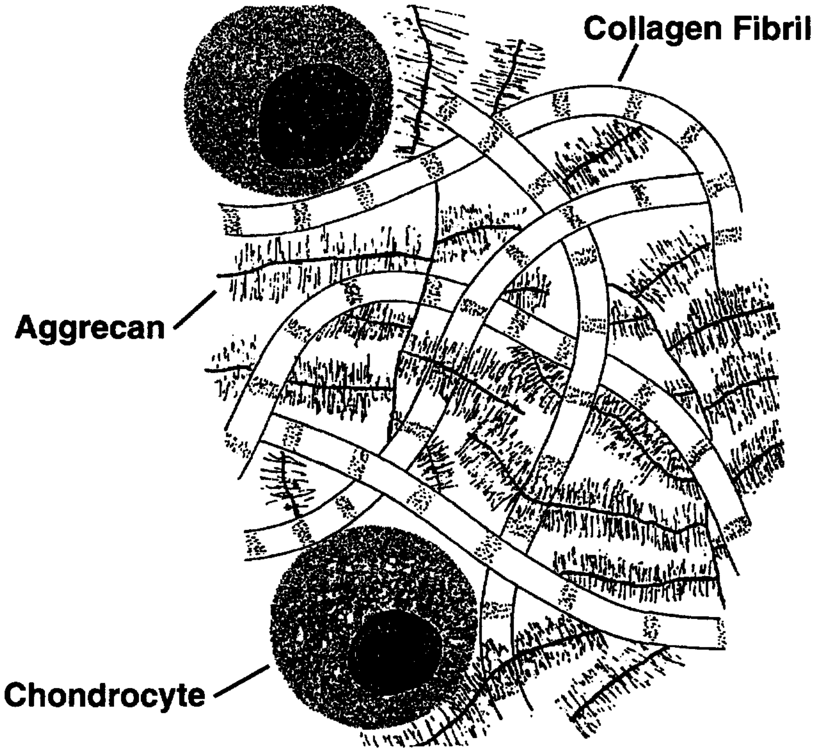

Fig. 1. Microstructural makeup of articular cartilage. The aggrecan molecules contain a large number of sulfated glycosaminoglycan subunits, which contribute to the highly negative fixed charge density of the solid matrix.

biological macromolecules (Fig. 1), primarily collagen fibrils and aggregated proteoglycans (or aggrecan). The proteoglycans contain a large number of sulfated glycosaminoglycan side chains which are negatively charged at physiological pH. Primarily due to these molecules, the solid matrix contains a high negative fixed (or immobile) charge density on the order of 0.2 M (Maroudas, 1979). Conversely, the interstitial fluid contains an excess of positively charged dissociated ions in order to maintain tissue electroneutrality at a macrocontinuum length scale. Microstructurally, these ions form electrical dipole layers (double-layers) with the fixed charge groups of the solid matrix. Because the microstructural arrangements of solid, fluid and ionic constituents must satisfy both microscopic and macroscopic mechanical, electrical and chemical balance laws, the macroscopic mechanical, electrical and chemical fluxes are all coupled. Manifestations of such coupling mechanisms include the phenomena of streaming potential and streaming current (mechanical-to-electrical), electroosmotic flow (electrical-to-mechanical) and osmotically induced swelling (chemical-to-mechanical).

A number of continuum theories have been used to describe these macroscopic couplings in membranes and biological tissues, including single continuum (Helfferich, 1962; Katchalsky and Curran, 1967; Eisenberg and Grodzinsky, 1987; Frank and Grodzinsky, 1987; Simon *et al.*, 1996) and multiple continuum mixture theory (Swenson, 1979; Lai *et al.*, 1991; Snijders *et al.*, 1992; Gu *et al.*, 1993; Huyghe and Janssen, 1997) approaches. Although analytical solutions are possible for simple geometries and material property distributions, treatment of more complex physical situations requires a numerical approach. Numerical implementations have been developed for problems in which boundary conditions are primarily mechanical or chemical in nature and macroscopic electric fields are assumed to have negligible impact (Snijders *et al.*, 1995; Simon *et al.*, 1996). Alternatively, linear (Lewis and Garner, 1972; Massé and Berthier, 1996) and finite deformation (Levenston *et al.*, 1997, 1998b) numerical approaches have been proposed for modeling electrokinetic coupling when boundary conditions are primarily mechanical or electrical in nature and macroscopic chemical concentration gradients negligibly impact the electromechanical phenomena of interest.

These previous formulations are applicable to a wide class of problems in the physics of biological tissues and other porous media. However, there are other situations in which both electrical and chemical effects are important. For example, modeling the transport of charged nutrients through articular cartilage might require simultaneous consideration of fluid flow, electric fields, chemical concentration gradients and finite deformations of the solid matrix. Although the general principles governing transport through charged membranes and tissues are well established (DeGroot and Mazur, 1969; Friedman, 1986: Helfferich, 1962; Katchalsky and Curran, 1967), most numerically implemented models have been restricted to one-dimensional problems with rigid or infinitesimally deformed solid matrices.

The goal of the present study was to develop a general variational framework for analysis of coupled fluid flow and solute transport in charged, deformable porous media under finite deformations. The variational approach allows us to derive local governing equations (e.g., conservation of momentum, electrochemical equilibrium conditions) that are fully consistent with our fundamental assumptions about material behavior. This consistency becomes important if, for example, we wish to introduce specific microstructural models for predicting interstitial solute behavior. Additionally, the variational approach naturally produces a framework suitable for numerical solution via the finite element method.

2. THEORY

2.1. *Continuum mechanics preliminaries*

Kinematic descriptions of porous media are often posed within the framework of continuum mixture theory, where the porous medium is treated as the superposition of two or more interacting continua simultaneously occupying the same physical space (Bowen, 1980; Kwan *et al.*, 1990; Thomas, 1991). In the present treatment, we adopt an alternate approach in the tradition of Biot (1972) and classical membrane biophysics (Katchalsky and Curran, 1967), viewing the porous medium as a single continuum defined by the boundaries of the solid matrix and considering average fluid (and solute) flow relative to the continuum. Under assumptions commonly invoked for biological tissues (e.g., immiscible, non-reactive, isothermal, quasistatic), the two finite deformation kinematic descriptions are mathematically equivalent (Simon, 1992; Levenston *et al.*, 1998b). As a preliminary, we state some standard definitions from continuum mechanics (Eringen, 1967; Marsden and Hughes, 1994).

Let the volume $\Omega_0 \subset \Re^3$ bounded by the surface Γ_0 be the Lagrangian reference configuration for the porous medium (see Remark 4) and let X indicate the material coordinates of a particle in Ω_0 (Fig. 2). Let the invertible deformation map from Ω_0 to the present Eulerian configuration Ω_t be denoted by $\varphi(X, t) : \Omega_0 \times [0, t] \to \Re^3$. The spatial position of a particle in Ω_t is given by:

$$x(X, t) = \varphi(X, t) = X + u(X, t) \tag{1}$$

where φ is a continuously differentiable, invertible mapping and u is the solid displacement. The invertible deformation gradient F and its Jacobian J are defined as:

$$F = \frac{\partial \varphi}{\partial X} \tag{2}$$

$$J = \det F \tag{3}$$

where J must be strictly positive to prohibit self-interpenetration of the continuum. The

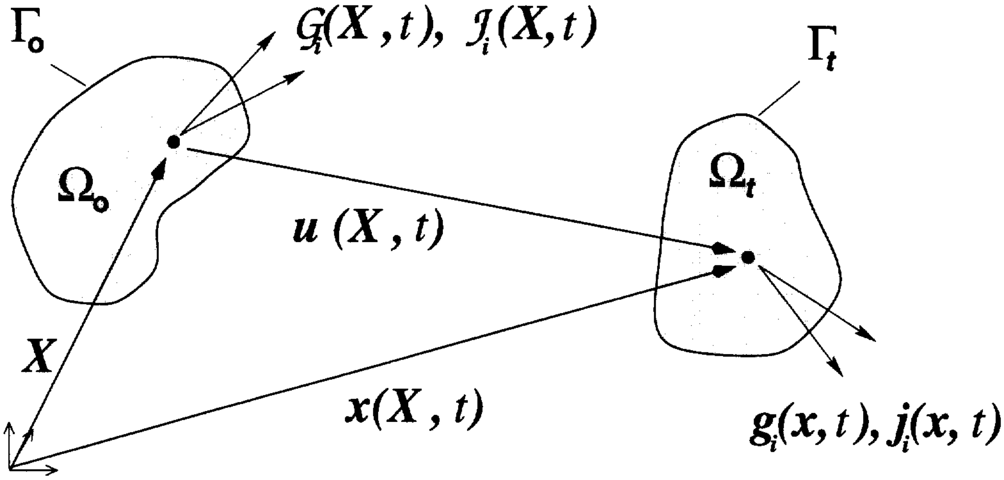

Fig. 2. Kinematic relationship between the Lagrangian reference configuration Ω_0 and the Eulerian configuration Ω_t.

right Cauchy–Green tensor A, Piola deformation tensor B and Lagrange strain tensor E are defined as:

$$A = F^T F \tag{4}$$

$$B = A^{-1} = F^{-1}F^{-T} \tag{5}$$

$$E = \tfrac{1}{2}(A - I) \tag{6}$$

where I is the rank-two identity tensor and the superscript T indicates transposition.

The spatial time derivative is defined as the partial time derivative holding the spatial position x fixed:

$$\frac{\partial}{\partial t} = \left.\frac{\partial}{\partial t}\right|_x . \tag{7}$$

Likewise, the material time derivative is defined as the partial time derivative holding the particle X fixed:

$$\dot{(\ )} = \frac{\mathrm{d}}{\mathrm{d}t} = \left.\frac{\partial}{\partial t}\right|_X = \frac{\partial}{\partial t} + v \cdot \nabla, \tag{8}$$

where the solid velocity $v = (\mathrm{d}x/\mathrm{d}t)$ is the material time derivative of the spatial position and ∇ is the Eulerian "del" operator. Finally, the convective time derivative of a vector g is defined as:

$$\overset{*}{g} = \frac{\partial g}{\partial t} + v \cdot (\nabla g) + g \nabla \cdot v - g \cdot (\nabla v). \tag{9}$$

This particular convective derivative accounts for volumetric deformation of the continuum, and is important when defining objective fluxes in a spatial frame relative to the deforming continuum (Eringen, 1967).

Although descriptions of the coupled flow phenomena of interest are naturally posed in the physical Eulerian configuration, numerical solutions of the governing equations are more conveniently carried out on a fixed Lagrangian reference configuration. It is, therefore, necessary to define and relate both Eulerian and Lagrangian forms of the macroscopic flux variables. Let $\boldsymbol{j}_i$ indicate the molar flux (i.e., moles/unit area/unit time) in Eulerian space of species i relative to the porous medium.[1] The molar flux $\mathcal{J}_i$ relative to the Lagrangian reference configuration is related to $\boldsymbol{j}_i$ by the Piola transformation:

$$\mathcal{J}_i = J\boldsymbol{F}^{-1}\cdot\boldsymbol{j}_i. \tag{10}$$

We now introduce Lagrangian and Eulerian molar "displacement densities" $\mathcal{G}_i$ and $\boldsymbol{g}_i$ such that:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{G}_i = \mathcal{J}_i, \tag{11}$$

$$\boldsymbol{g}_i = \frac{1}{J}\boldsymbol{F}\cdot\mathcal{G}_i \tag{12}$$

One can then determine that $\boldsymbol{j}_i = \overset{*}{\boldsymbol{g}}_i$. Physically, $\mathcal{G}_i$ represents the net molar transport of species i through a unit reference area since the medium "left" the reference state. We can thus define the Lagrangian molar concentration of species i as:

$$\mathcal{C}_i = \mathcal{C}_i^0 - \mathrm{DIV}\,\mathcal{G}_i, \tag{13}$$

where $\mathcal{C}_i^0$ is the concentration in the reference state[2] and DIV is the Lagrangian divergence operator. The corresponding Eulerian molar concentration c_i is given by the Piola identity, which accounts for the local volume change of the continuum:

$$c_i = \frac{1}{J}\mathcal{C}_i = c_i^0 - \nabla\cdot\boldsymbol{g}_i. \tag{14}$$

Analogous definitions can be posed for any other flux variable. For example, we denote by $\overset{*}{\boldsymbol{w}}$ the Eulerian volumetric fluid flux relative to the solid (also known as the "relative fluid velocity" in some poroelastic formulations).[3] Consequently, we can define the Lagrangian relative fluid flux as:

$$\dot{\mathcal{W}} = J\boldsymbol{F}^{-1}\cdot\overset{*}{\boldsymbol{w}}. \tag{15}$$

We also define ξ as the change in fluid volume content relative to the Lagrangian reference configuration:

$$\xi = -\mathrm{DIV}\,\mathcal{W}, \tag{16}$$

where $\mathcal{W}$ can be though of as the Lagrangian relative fluid displacement.

Remark 1. It is important to realize that the concentrations C_i and c_i represent the molar content per unit volume of the porous medium as a whole. The average interstitial concentration (moles per unit fluid volume) $\bar{c}_i$ is given by:

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[1] It is important to note that in the present formulation, we consider the macroscopic, continuum averaged flux of a species relative to the continuum as a whole, not the microscopic flux within the matrix interstitial spaces.

[2] An important distinction must be made between the reference configuration and the reference state. To fully specify the stress-free reference state, we must specify both the kinematic configuration and the solute concentrations in this state, as changes in chemical composition may induce a matrix stress without any matrix deformation. The reference configuration is the kinematic configuration corresponding to the reference state for the medium. If solute is removed from the medium, the concentration $\mathcal{C}_i$ in the reference configuration (i.e., moles per unit undeformed volume) will decrease below the reference state concentration $\mathcal{C}_i^0$.

[3] Strictly speaking, a distinction should be drawn between the fluid velocity and the solvent velocity. In general, the fluid velocity includes the volumetric flux of the solvent and all solute species. We assume in the present formulation that the partial volumes of all solute species are negligible, which implies that the solute velocity and fluid velocity are equivalent.

$$\bar{c}_i = \frac{c_i}{\phi^f}, \tag{17}$$

where ϕ^f is the fluid volume fraction. We treat the medium as fully saturated, so:

$$\phi^f + \phi^s = 1, \tag{18}$$

where ϕ^s is the solid volume fraction. Because the solid is treated as intrinsically incompressible, both the solid and fluid volume fractions are direct functions of the volumetric deformation:

$$\phi_s = \frac{\phi_0^s}{J}, \tag{19}$$

$$\phi^f = 1 - \phi^s = \frac{J - 1 + \phi_0^f}{J}, \tag{20}$$

where ϕ_0^s and ϕ_0^f are the solid and fluid volume fractions in the Lagrangian reference configuration, respectively. The relationship between the continuum averaged concentration c_i and the average interstitial concentration $\bar{c}_i$, therefore, depends on the deformation state of the medium.

There are situations in which all of the fluid may not be accessible to all solute species. For example, the intrafibrillar fluid within the collagen fibrils of articular cartilage may not be accessible to large solutes that cannot penetrate the fibrils (Maroudas, 1979). This could be accounted for by explicitly including the intrafibrillar fluid as a separate component in the balance equations. The present treatment is restricted to cases where the solvent is fully available to all solutes.

2.2. *Variational framework*

In the subsequent sections, we motivate our theoretical formulation within the variational framework of the principle of virtual power (Penfield and Haus, 1967; Maugin and Eringen, 1977). In order to implement the variational approach, we first describe the porous medium thermodynamically in terms of energy flow and subsequently derive local governing equations (e.g., conservation of momentum, electrochemical equilibrium, etc.) from this description. Although this approach is somewhat abstract in that local equations are not directly specified, it ensures that the derived local equations are fully consistent with any assumptions about material behavior built into the variational description. Likewise, any changes in the basic assumptions will be consistently represented in the local equations.

We will first define a power balance functional Ψ for the porous medium:

$$\Psi(\boldsymbol{d}, \dot{\boldsymbol{d}}) = \frac{\mathrm{d}}{\mathrm{d}t} E^{\mathrm{int}} + P^{\mathrm{diss}} - P^{\mathrm{ext}} \tag{21}$$

where E^{int} is the Helmholtz free energy of the medium, P^{diss} is the dissipative power, and P^{ext} is the external power supplied across the boundary. We consider Ψ to depend on the independent variables $\boldsymbol{d}$ and their time derivatives (or generalized velocities) $\dot{\boldsymbol{d}}$. In addition to requiring that Ψ itself be identically zero (as implied by the first law of thermodynamics), we require the first variation of Ψ in a generalized virtual velocity field to vanish:

$$\delta\Psi = \frac{\partial}{\partial\eta} \Psi(\boldsymbol{d}, \dot{\boldsymbol{d}} + \eta\delta\dot{\boldsymbol{d}})\,|_{\eta=0} = 0, \tag{22}$$

where the virtual velocities $\delta\dot{\boldsymbol{d}}$ represent arbitrary admissible variations in $\dot{\boldsymbol{d}}$ and η is an arbitrarily small parameter. For a non-equilibrium open system, this condition is analogous to requiring the first variation of the Gibbs free energy to be zero for thermodynamic equilibrium of a closed system. Enforcement of eqn (22) will directly imply the local governing equations.

To apply this formulation to a given physical system, we must identify appropriate forms of E^{int}, P^{diss} and P^{ext}, as well as a consistent set of independent variables $\boldsymbol{d}$. In the present context, these functionals will combine contributions related to the solid matrix, the interstitial fluid and each solute species. Additionally, we will introduce continuum phenomenological coupling laws of nonequilibrium thermodynamics to describe interactions between the system components.

2.3. *Mechanical poroelastic formulation*

We previously utilized the principle of virtual power to generate a three-field mixed poroelastic formulation appropriate for finite deformation analysis when macroscopic chemical and electrical phenomena negligibly influence the mechanical response (Levenston *et al.*, 1998a). In that formulation, we modeled quasistatic deformations of an isothermal,[4] saturated porous medium with intrinsic incompressibility of both solid and fluid constituents. The combination of the saturation condition [eqn (18)] with intrinsic constituent incompressibility produces a constraint on the relationship between bulk and fluid dilatations:

$$J-1-\xi=0. \tag{23}$$

Thus, volumetric deformation $(J-1)$ of an initially undeformed region must be accomplished via a change (ξ) in the fluid volume content.

By introducing the scalar fluid pressure p and treating it as a Lagrange multiplier enforcing the saturation/constituent incompressibility constraint [eqn (23)], we formulated the Helmholtz free energy of the porous medium as:

$$E^{\text{int}}_{\text{pe}}=\int_{\Omega_0}[U_{\text{pe}}(A)-p(J-1-\xi)]\,\mathrm{d}\Omega. \tag{24}$$

The hyperelastic stored energy density $U_{\text{pe}}(A)$ (defined on the Lagrangian configuration) represents the energy stored through deformation of the solid matrix irrespective of any fluid pressurization.[5] Likewise, we wrote the dissipative and external powers as:

$$P^{\text{diss}}_{\text{pe}}=-\int_{\Omega_0}\text{GRAD}\,p\cdot\mathcal{W}\,\mathrm{d}\Omega \tag{25}$$

$$P^{\text{ext}}_{\text{pe}}=\int_{\Gamma_0}(\boldsymbol{f}\cdot\boldsymbol{v}-p\mathcal{W}\cdot\boldsymbol{N})\,\mathrm{d}\Gamma \tag{26}$$

where GRAD is the Lagrangian gradient operator and $\boldsymbol{f}$ and $\boldsymbol{N}$ are, respectively, the traction and surface normal vectors defined on the Lagrangian boundary Γ_0.

We completed the poroelastic formulation by combining eqns (21), (24), (25) and (26) and explicitly introducing Darcy's law (defined in the Eulerian configuration) relating fluid flow to the pressure gradient:

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[4] We assume that the dissipation rate is small in comparison with the characteristic thermal conduction rate and that the medium resides in an infinite bath of constant temperature (typically, ≈37°C for biological systems). Thus, we do not explicitly model the heat conduction "subsystem", and instead assume that the system remains isothermal.

[5] For a porous medium with compressible constituents, the "total" energy density would be the sum of $U_{\text{pe}}(A)$ and a term describing the energy stored through dilatation of the individual constituents by the fluid pressure. Because we treat both the solid and fluid constituents as incompressible, this second term becomes $p(J-1-\xi)$, an energy of constraint which is identically zero. See Simon (1992) or Levenston *et al.* (1998a) for a more thorough discussion of this point.

$$\overset{*}{\boldsymbol{w}} = -\boldsymbol{k}_d(A) \cdot \nabla p, \tag{27}$$

where $\boldsymbol{k}_d$ is the deformation-dependent rank-two permeability tensor. For a total Lagrangian formulation, we considered $(\boldsymbol{u}, \mathscr{W}, p)$ to be the set of independent variables, with $(\delta \boldsymbol{v}, \delta \dot{\mathscr{W}}, \delta)$ as the corresponding generalized virtual velocities. In the following section, we develop generalized definitions of E^{int}, P^{diss} and P^{ext} that incorporate chemical and electrical effects due to the presence of charged and uncharged solute species.

2.4. *Physicochemical poroelastic formulation*

In order to extend the mechanical formulation to account for electrochemical effects, we must generate an analogous macroscopic energetic description governing the flow of charged and uncharged solutes. Before doing so, we will introduce some physicochemical concepts describing the thermodynamics of solutions.

At any point in a solution, the Helmholtz free energy density e_i^s associated with solute species i is defined as (Guggenheim, 1977):

$$e_i^s = c_i^s[\mu_i^0(T) + RT(\ln a_i^s - 1) + z_i \mathscr{F} \Phi^s], \tag{28}$$

where c_i^s is the molar concentration (moles/unit volume) of species i, $\mu_i^0(T)$ is a function of the absolute temperature T, R is the universal gas constant, a_i^s is the "activity" of species i, z_i is the valence of species i, $\mathscr{F}$ is the Faraday constant and Φ^s is the electrical potential. The superscript s indicates a local value in the solution, which may be a free solution or the fluid within the interstices of a porous medium. We treat the medium as isothermal in the present study, so μ_i^0 is a constant. Note that z_i accounts for both the sign and number of charges per solute molecule. The activity a_i^s represents the "effective" concentration of species i in a non-ideal solution:

$$a_i^s = \gamma_i^s c_i^s, \tag{29}$$

where the activity coefficient γ_i^s describes the deviation from the behavior in an ideal, infinitely dilute solution. In general, the activity coefficient includes the net effect of interactions with all solutes in a solution (e.g., electrostatic effects, solvation, etc.), and thus depends on the concentration of all solute species.

The scalar electrochemical potential v_i^s can be defined thermodynamically as the incremental increase in the internal energy density of a system accompanying an incremental increase in the molar concentration of species i:[6]

$$v_i^s = \frac{\partial e_i^s}{\partial c_i^s}. \tag{30}$$

The spatial gradient of v_i can be thought of as the "driving force" for the flux of species i, just as the pressure gradient is the driving force for fluid flow. The electrochemical potential for a solute in a simple solution is thus given by:

$$v_i^s = \mu_i^0 + RT \ln a_i^s + z_i \mathscr{F} \Phi^s. \tag{31}$$

The chemical potential μ_i^s for a given solute is given by:

$$\mu_i^s = \mu_i^0 + RT \ln(a_i^s). \tag{32}$$

For a neutral solute, the electrochemical and chemical potentials are identical. More generally, the electrochemical and chemical potentials would include terms related to the

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[6] The electrochemical potential is more often derived from $v_i = (\partial G/\partial n_i)$, where G is the Gibbs free energy of the system and n_i is the total number of moles of species i.

partial volumes of the species, but we have already assumed that the partial volumes of all solute species are negligible.

Remark 2. Within the interstitial fluid of a porous medium, the actual distributions of the solutes may be highly nonuniform (e.g., due to significant double-layer effects). In this case, we can define the average energy density associated with species i an average of e_i over a characteristic "microcontinuum" region of fluid Ω_{micro}:

$$\bar{e}_i = \frac{\int_{\Omega_{\text{micro}}} e_i^s \, \mathrm{d}\Omega}{\int_{\Omega_{\text{micro}}} \mathrm{d}\Omega}. \tag{33}$$

Evaluation of $\bar{e}_i$ with this approach requires the use of a microcontinuum model to predict the microscopic distributions of solute concentrations and the electrical potential. For example, Ω_{micro} could represent the unit cell volume in the Poisson–Boltzmann micromodel of Buschmann and Grodzinsky (1995). Although not necessarily tractable in closed form, theoretically the "effective" electrochemical potential for the interstitial fluid could then be determined as:

$$\bar{v}_i = \frac{\partial \bar{e}_i}{\partial \bar{c}_i}, \tag{34}$$

where the average interstitial concentration is:

$$\bar{c}_i = \frac{\int_{\Omega_{\text{micro}}} c_i^s \, \mathrm{d}\Omega}{\int_{\Omega_{\text{micro}}} \mathrm{d}\Omega}. \tag{35}$$

The microscopic solute distributions and macroscopic solute fluxes are linked via eqns (14), (17) and (35).

The inhomogeneous microstructural solute distributions resulting from the double layer effects will cause the macroscopic behavior to deviate from predictions based on the average interstitial solute concentrations and potentials. To simplify the subsequent analysis, we will assume as a first order approximation that any such deviations are negligible. This assumption is consistent with the classic Donnan macromodel for ion exchange systems (Helfferich, 1962). We will also assume that the activity coefficients do not change appreciably over the solute concentration ranges of interest. These two assumptions are accurate for many biological tissues and membranes (Friedman, 1986). Although we consider the $\bar{\gamma}_i$ to be constant within the tissue, we do not require that they equal the values in free solution. While the coupled macro-microcontinuum approach outlined above is mathematically more complicated, implementation of such an approach would proceed by direct analogy to the following derivation.

Given the preceding assumptions, the partial Helmholtz energy for solute species i in the porous medium can be expressed as an integral over the reference configuration:

$$E_i^{\text{int}} = \int_{\Omega_0} C_i[\mu_i^0 + RT(\ln \bar{a}_i - 1) + z_i \mathscr{F} \Phi] \, \mathrm{d}\Omega. \tag{36}$$

In other words, we now express the partial Helmholtz energy as an integral of the energy density per unit tissue volume in the reference configuration. Combining the mechanical energy [eqn (24)] with the electrochemical energy of the solute species, we can now write the total free energy for the porous medium as:

$$E^{\mathrm{int}} = \int_{\Omega_0} \left[U(A, C_1, \ldots, C_n) - p(J - 1 - \xi) + \sum_i C_i(\bar{\mu}_i - RT) + \Phi \left(\rho_{m_0} + \mathscr{F} \sum_i z_i C_i \right) \right] \mathrm{d}\Omega. \tag{37}$$

Note that we have also introduced the term $\Phi\rho_{m_0}$ representing the electrostatic energy density associated with raising the matrix fixed charge to a given macroscopic electrical potential. The matrix fixed charge density ρ_{m_0} is expressed as the charge per unit tissue volume in the reference configuration. For simplicity, we assume that ρ_{m_0} is a constant, but titration of fixed charge groups with changes in interstitial pH could easily be accounted for. We subsequently treat Φ as an independent Lagrange multiplier that enforces a macroscopic electroneutrality constraint:

$$\rho_0 = \rho_{m_0} + \mathscr{F} \sum_i z_i C_i = 0, \tag{38}$$

where ρ_0 is the net macroscopic charge density for the continuum. Although we have not explicitly defined the Helmholtz energy density of the solvent in terms of its chemical potential, such a definition is implicitly incorporated through the term $p\xi$ in eqn (37). Note that we now treat the hyperelastic energy density $U(A, C_1, \ldots, C_n)$ as a function of both the deformation and the solute concentrations. By doing so, we allow the elastic behavior of the solid skeleton at a given deformation state to change depending on the interstitial solution composition (Eisenberg and Grodzinsky, 1985). As we will see in Section 2.6, this dependency influences the chemical equilibrium conditions for the material.

Remark 3. In a purely mechanical formulation, interpretation of the fluid pressure p as the hydrostatic pressure is straightforward. In a formulation that includes osmotic effects, however, the fluid pressure must be carefully interpreted to avoid confusion. In the present treatment, p represents the apparent fluid pressure, which can be decomposed as follows (Katchalsky and Curran, 1967):

$$p = p_{\mathrm{hyd}} - \pi, \tag{39}$$

where p_{hyd} is the hydrostatic fluid pressure and π is the osmotic pressure. For an ideal solution:

$$\pi = RT \sum_i \bar{c}_i. \tag{40}$$

If the actual behavior of the interstitial solution is not accurately represented by predictions based on the average concentrations, then the true osmotic pressure will differ from that predicted by eqn (40) and, like the energy density, could be predicted via a microcontinuum averaging approach. The notion of an apparent pressure p incorporating both mechanical and physicochemical components is motivated by the fact that gradients in both hydrostatic and osmotic pressures are capable of inducing fluid flow. One could also derive the apparent pressure p from the chemical potential of the solvent as the potential whose gradient is thermodynamically conjugate to the solute volumetric flux. In a purely mechanical formulation (Section 2.3), chemical concentration gradients (and therefore osmotic pressure gradients) are assumed to be negligible, so p and p_{hyd} are identical to within an arbitrary constant. In the present study, we treat p as a Lagrange multiplier variable and p_{hyd} as a derived quantity.

The dissipative power, representing the net rate of irreversible energy loss (or conversion to entropy), is defined in terms of the various fluxes and their thermodynamically conjugate "forces" (DeGroot and Mazur, 1969; Katchalsky and Curran, 1967):

$$P^{\text{diss}} = \int_{\Omega_0} -\left(\mathscr{W}\cdot\text{GRAD}\,p + \sum_i \mathscr{J}_i\cdot\text{GRAD}\,\bar{\nu}_i\right)\mathrm{d}\Omega, \tag{41}$$

where the pressure and potential gradients are forces in the thermodynamic sense. Note that individual terms in the integrand of eqn (41) may be negative so long as the net dissipation for the medium is non-negative (i.e., the rate of entropy production is strictly non-negative). As with the free energy, the macrocontinuum dissipative power could be computed using a microcontinuum averaging approach (Happel, 1959; Basser and Grodzinsky, 1993; Chammas *et al.*, 1994), and would be reflected in the phenomenological coupling coefficients of Section 2.5.

Finally, the external power supply represents the sum of the influences of the external environment on each component of the system:

$$P^{\text{ext}} = \int_{\Gamma_0}\left[\boldsymbol{f}\cdot\boldsymbol{v} - \left(p\mathscr{W} + \sum_i \nu_i \mathscr{J}_i\right)\cdot\boldsymbol{N}\right]\mathrm{d}\Omega. \tag{42}$$

Thus, the net power supply includes the power associated with the net boundary traction acting on a moving boundary, the apparent pressure forcing fluid flow across the boundary, and the individual electrochemical potentials forcing solute fluxes across the boundary.

2.5. *Nonequilibrium thermodynamic coupling*

To complete the purely mechanical poroelastic formulation, we introduced Darcy's law [eqn (27)] to relate the fluid velocity and pressure gradient. In an analogous manner, we complete the present formulation by introducing a phenomenological coupling law relating the fluxes $\overset{*}{\boldsymbol{w}}$ and $\boldsymbol{j}_i$ to their thermodynamically conjugate forces. For a system including n solute species (DeGroot and Mazur, 1969; Katchalsky and Curran, 1967):

$$\begin{Bmatrix} \overset{*}{\boldsymbol{w}} \\ \boldsymbol{j}_1 \\ \vdots \\ \boldsymbol{j}_n \end{Bmatrix} = \begin{bmatrix} \boldsymbol{l}_{ff} & \boldsymbol{l}_{f1} & \cdots & \boldsymbol{l}_{fn} \\ \boldsymbol{l}_{1f} & \boldsymbol{l}_{11} & \cdots & \boldsymbol{l}_{1n} \\ \vdots & \vdots & \ddots & \vdots \\ \boldsymbol{l}_{nf} & \boldsymbol{l}_{n1} & \cdots & \boldsymbol{l}_{nn} \end{bmatrix} \begin{Bmatrix} \nabla p \\ \nabla\bar{\nu}_1 \\ \vdots \\ \nabla\bar{\nu}_n \end{Bmatrix}, \tag{43}$$

where the $\boldsymbol{l}_{ij}$ are rank-two coupling tensors that may vary with deformation, concentration, etc. Thus, the first line represents a generalized Darcy's law and the other lines represent generalized electrodiffusion equations. Note that the gradient of the electric potential Φ is intrinsically incorporated via the electrochemical potential gradients of any ionic solutes. These coupling coefficients have been physically interpreted in terms of frictional drag between members of the different constituents (Katchalsky and Curran, 1967). Note that the subscript "f" indicates a quantity related to the fluid constituent. Onsager's reciprocity theorem (DeGroot and Mazur, 1969) is a basic theorem of nonequilibrium thermodynamics that can be derived from statistical thermodynamic arguments using the property of "time reversal invariance". In essence, this principal states that the macroscopic coupling matrix in eqn (43) is symmetric. Consequently, the on-diagonal tensors $\boldsymbol{l}_{ii}$ are symmetric, and $\boldsymbol{l}_{ij} = \boldsymbol{l}_{ji}^{T}$. The number of independently determined tensors could be further reduced by introducing additional constitutive laws for the species fluxes (see Appendix A).

The phenomenological coupling law can be posed in an equivalent Lagrangian form as:

$$\begin{Bmatrix} \dot{\mathcal{W}} \\ \mathcal{J}_1 \\ \vdots \\ \mathcal{J}_n \end{Bmatrix} = \begin{bmatrix} \boldsymbol{L}_{ff} & \boldsymbol{L}_{f1} & \cdots & \boldsymbol{L}_{fn} \\ \boldsymbol{L}_{1f} & \boldsymbol{L}_{11} & \cdots & \boldsymbol{L}_{1n} \\ \vdots & \vdots & \ddots & \vdots \\ \boldsymbol{L}_{nf} & \boldsymbol{L}_{n1} & \cdots & \boldsymbol{L}_{nn} \end{bmatrix} \begin{Bmatrix} \mathrm{GRAD}\, p \\ \mathrm{GRAD}\, \bar{v}_1 \\ \vdots \\ \mathrm{GRAD}\, \bar{v}_n \end{Bmatrix}, \tag{44}$$

where the Lagrangian forms of the coupling tensors are given by:

$$\boldsymbol{L}_{ij} = J\boldsymbol{F}^{-1}\boldsymbol{l}_{ij}\boldsymbol{F}^{-T}. \tag{45}$$

Inversion of eqn (44) leads to expressions for the Lagrangian thermodynamic forces:

$$\begin{Bmatrix} \mathrm{GRAD}\, p \\ \mathrm{GRAD}\, \bar{v}_1 \\ \vdots \\ \mathrm{GRAD}\, \bar{v}_n \end{Bmatrix} = \begin{bmatrix} \boldsymbol{R}_{ff} & \boldsymbol{R}_{f1} & \cdots & \boldsymbol{R}_{fn} \\ \boldsymbol{R}_{1f} & \boldsymbol{R}_{11} & \cdots & \boldsymbol{R}_{1n} \\ \vdots & \vdots & \ddots & \vdots \\ \boldsymbol{R}_{nf} & \boldsymbol{R}_{n1} & \cdots & \boldsymbol{R}_{nn} \end{bmatrix} \begin{Bmatrix} \dot{\mathcal{W}} \\ \mathcal{J}_1 \\ \vdots \\ \mathcal{J}_n \end{Bmatrix}. \tag{46}$$

2.6. *Variational equation for physicochemical poroelasticity*

The power balance functional Ψ is now obtained by combining eqns (21), (37), (41) and (42). We consider $(\boldsymbol{u}, \mathcal{W}, \mathcal{G}_i, p, \Phi)$ to be the set of independent variables, with $(\delta\boldsymbol{v}, \delta\dot{\mathcal{W}}, \delta\mathcal{J}_i, \delta\dot{p}, \delta\dot{\Phi})$ as the corresponding set of generalized virtual velocities. We now explicitly introduce eqn (46) and require the first variation of Ψ with respect to the generalized virtual velocities to vanish:

$$\frac{\partial}{\partial\eta}\Psi(\boldsymbol{u}, \mathcal{W}, \mathcal{G}_i, p, \Phi, \boldsymbol{v}+\eta\delta\boldsymbol{v}, \dot{\mathcal{W}}+\eta\delta\dot{\mathcal{W}}, \mathcal{J}_i+\eta\delta\mathcal{J}_i, \dot{p}+\eta\delta\dot{p}, \dot{\Phi}+\eta\delta\dot{\Phi})|_{\eta=0} = 0. \tag{47}$$

This produces the following variational equation:

$$\begin{aligned} \int_{\Omega_0} \Bigg\{ &[\boldsymbol{S}^e - (p+\pi)J\boldsymbol{B}] : \delta\dot{\boldsymbol{E}} + p\delta\dot{\xi} - \delta\dot{p}(J-1-\xi) + \sum_i \left[\bar{v}_i + \frac{\partial U(\boldsymbol{A}, C_1, \ldots, C_n)}{\partial C_i}\right]\delta\dot{C}_i \\ &+ \delta\dot{\Phi}\left(\rho_{m_0} + \mathcal{F}\sum_i z_i C_i\right) + \delta\dot{\mathcal{W}}\cdot\left(\boldsymbol{R}_{ff}\cdot\dot{\mathcal{W}} + \sum_i \boldsymbol{R}_{fi}\cdot\mathcal{J}_i\right) \\ &+ \sum_k \delta\mathcal{J}_k\cdot\left(\boldsymbol{R}_{kf}\cdot\dot{\mathcal{W}} + \sum_i \boldsymbol{R}_{ki}\cdot\mathcal{J}_i\right)\Bigg\}\mathrm{d}\Omega - \int_{\Gamma_0}\left(\boldsymbol{f}\cdot\delta\boldsymbol{v} - p\boldsymbol{N}\cdot\delta\dot{\mathcal{W}} - \sum_i \bar{v}_i\boldsymbol{N}\cdot\delta\mathcal{J}_i\right)\mathrm{d}\Gamma = 0, \end{aligned} \tag{48}$$

where $\delta\dot{\boldsymbol{E}}$, $\delta\dot{\xi}$ and $\delta\dot{C}_i$ are defined consistently with $\delta\boldsymbol{v}$, $\delta\dot{\mathcal{W}}$ and $\delta\mathcal{J}_i$, respectively, and the elastic (or "extra") second Piola–Kirchoff stress tensor $\boldsymbol{S}^e$ is defined as:

$$\boldsymbol{S}^e = \frac{\partial U(\boldsymbol{A}, C_1, \ldots, C_n)}{\partial \boldsymbol{E}}. \tag{49}$$

As the virtual velocities are arbitrary and independent, eqn (48) implies the local

Table 1. Local equations implied by the global variational equation [eqn (48)] for a physicochemically coupled poroelastic medium

Linear momentum balance	$\mathrm{DIV}\,\boldsymbol{T} = \boldsymbol{0}$ in Ω_0
Mass conservation	$J-1-\xi = 0$ in Ω_0
Charge conservation	$\rho_{m_0}+\mathscr{F}\sum_i z_i C_i = 0$ in Ω_0
Generalized Darcy's law	$\mathrm{GRAD}\,p-\boldsymbol{R}_{ff}\cdot\dot{\mathscr{W}}-\sum_i \boldsymbol{R}_{fi}\cdot\mathscr{J}_i = \boldsymbol{0}$ in Ω_0
Generalized electrodiffusion equation	$\mathrm{GRAD}\,\tilde{v}_k-\boldsymbol{R}_{kf}\cdot\dot{\mathscr{W}}-\sum_i \boldsymbol{R}_{ki}\cdot\mathscr{J}_i = \boldsymbol{0}$ in Ω_0
Traction boundary condition	$\boldsymbol{N}\cdot\boldsymbol{T}-\boldsymbol{f} = \boldsymbol{0}$ on Γ_{0_σ}
Pressure boundary condition	$p-\hat{p} = 0$ on Γ_{0_p}
Electrochemical boundary condition	$\tilde{v}_i-\hat{v}_i = 0$ on $\Gamma^i_{0_v}$

Note that $\hat{p}$ and $\hat{v}_i$ are values prescribed on portions of the boundary and the apparent electrochemical potential $\tilde{v}_k$ and total first Piola–Kirchhoff stress $\boldsymbol{T}$ are defined in the text [eqns (50) and (51)]. The reference configuration must be defined such that the mass and charge conservation constraints are initially satisfied.

equations shown in Table 1. Note that we have now defined an apparent electrochemical potential $\tilde{v}_i$ reflecting the additional influence of the chemically dependent solid strain energy density:

$$\tilde{v}_i = \bar{v}_i+\frac{\partial U(\boldsymbol{A}, C_1, \ldots, C_n)}{\partial C_i} \tag{50}$$

Additionally, we have defined the total first Piola–Kirchhoff stress $\boldsymbol{T}$ as:

$$\boldsymbol{T} = [\boldsymbol{S}^e-(p+\pi)J\boldsymbol{B}]\cdot\boldsymbol{F}^T = \boldsymbol{T}^e-(p+\pi)J\boldsymbol{F}^{-1}. \tag{51}$$

The osmotic pressure π in the expression for the total stress arises from the implicit dependence (via $\bar{c}_i$) of the solute free energy densities on the volumetric deformation:

$$\frac{\partial}{\partial \boldsymbol{E}}\sum_i C_i(\bar{v}_i-RT) = -\left[\sum_i \bar{c}_i\left(\sum_k \frac{\partial \bar{v}_i}{\partial \bar{c}_k}\bar{c}_k\right)\right]J\boldsymbol{B} = -\pi J\boldsymbol{B}. \tag{52}$$

In the present treatment, the bracketed term equals the interstitial osmotic pressure calculated via eqn (40). However, as discussed in Remark 3, π may take a different functional form if our assumptions about solute behavior change (e.g., if a given electrochemical potential functionally depends on the concentrations of all solutes). Regardless, the π in eqn (51) will exactly equal the π in the definition of the apparent pressure [eqn (39)], leaving $\boldsymbol{T} = \boldsymbol{T}^e-p_{\text{hyd}}J\boldsymbol{F}^{-1}$ as the total first Piola–Kirchhoff stress. The corresponding total Cauchy stress is $\boldsymbol{\sigma} = \boldsymbol{\sigma}^e-p_{\text{hyd}}\boldsymbol{I}$.

Table 1 presents a consistent and complete set of equations governing the behavior of the coupled medium. We now require only the specification of specific constitutive relations, geometry, boundary conditions, and admissible initial conditions for a fully posed problem.

In this formulation, we must specify boundary conditions on Γ_0 for the porous medium as a whole. Thus, we must prescribe either the solid displacement $\boldsymbol{u}$ and corresponding velocity $\boldsymbol{v}$ on Γ_{0_u} or the traction $\boldsymbol{f}$ on Γ_{0_σ}, where Γ_{0_u} and Γ_{0_σ} are complementary portions of Γ_0:

$$\Gamma_0 = \Gamma_{0_u}\cup\Gamma_{0_\sigma}, \quad \Gamma_{0_u}\cap\Gamma_{0_\sigma} = \varnothing. \tag{53}$$

Likewise, we must prescribe either the relative fluid displacement $\mathscr{W}$ and corresponding relative fluid velocity $\dot{\mathscr{W}}$ on Γ_{0_w} or the apparent pressure p on Γ_{0_p}, where Γ_{0_w} and Γ_{0_p} are also complementary portions of Γ_0. Finally, for each solute species we must prescribe either the relative molar displacement density $\mathcal{G}_i$ and corresponding relative molar flux $\mathcal{J}_i$ on $\Gamma^i_{0_g}$ or the electrochemical potential ν_i on $\Gamma^i_{0_\nu}$, where $\Gamma^i_{0_g}$ and $\Gamma^i_{0_\nu}$ too are complementary portions of Γ_0. These boundary partitions apply to each vectorial component of the displacements and displacement densities, so mixed boundary conditions are admissible. In general, the solid, fluid, and electrochemical boundary partitions need not coincide. If the external bathing solution is not well mixed, these prescribed boundary conditions must also account for the effects of unstirred boundary layers.

Remark 4. It is appropriate now to revisit the concept of an "undeformed" Lagrangian reference configuration Ω_0 for the porous medium. The choice of this configuration is not trivial, as the external environment must be accounted for. One choice for the reference configuration is the mechanically unloaded state corresponding to a hypothetical bathing solution with infinite solute concentration. In this hypothetical configuration, the internal and external osmotic pressures (see Remark 3) will be equivalent and the elastic stress will be zero. Consequently, a mechanically unloaded sample in equilibrium with a "physiological" bathing solution will be deformed relative to this reference configuration (i.e., $\boldsymbol{x} \neq \boldsymbol{X}$), the internal and external osmotic pressures will be different, and the elastic stress will be non-zero.

Although this hypothetical reference state is mathematically appealing, it is often more physically convenient to choose a physiological reference state when studying biological tissues. An alternative is to consider a mechanically unloaded specimen in a physiological bathing solution to be in its reference state. This choice, however, requires the elastic stress to be non-zero in the undeformed reference state. This elastic pre-stress must be accounted for when defining the Helmholtz energy density function for the solid. We note that any well-defined reference state is equally acceptable mathematically, so long as the implications of that choice (e.g., the pre-stress) are consistently accounted for.

3. SPECIFIC EXAMPLES

For problems in which we wish to specify the solute concentrations or electrical potential along part or all of the boundary, the formulation represented by eqn (55) is convenient, and can be directly implemented numerically. Although situations in which we would want to specify the flux of one or both ionic species are rare, such an implementation would also be appropriate for these applications. It is generally more convenient to prescribe the species concentration and electrical potential on a boundary than it is to prescribe the electrochemical potential as a whole. As the concentration and electrical potential uniquely determine the electrochemical potential, this poses no practical difficulty. However, the imposition of a prescribed electrical current density on the boundary is somewhat problematic. In a system where the electrical current is produced by ionic fluxes, the current density $\boldsymbol{j}_{el}$ is defined as:

$$\boldsymbol{j}_{el} = \mathcal{F} \sum_i z_i \boldsymbol{j}_i. \tag{54}$$

Thus, if we wish to prescribe the current density on the boundary without prescribing the individual species fluxes, we must somehow implement an additional constraint on the relationship between the boundary fluxes of all ionic solutes. For example, this could be achieved in a numerical implementation by introducing additional constraint equations (and corresponding Lagrange multiplier variables) relating the flux degrees of freedom on the appropriate boundary sections.

As an alternative, it may be more convenient to use eqn (47) and the preceding development as a framework for physically describing the system and then to reformulate the problem in terms of a new, thermodynamically consistent set of fluxes and potentials (Katchalsky and Curran, 1967). The new fluxes must be linearly independent of each other, and must uniquely determine all of the species fluxes (including the fluid velocity) in the original formulation. Such a mathematical reformulation is conducted as a matter of convenience, and we will not necessarily view the new variables as physically meaningful quantities. If we consistently define the new fluxes and potentials, we will always be able to recover the actual ion fluxes as a postprocessing operation. The following two examples will illustrate this approach.

3.1. *Example* 1 : *Binary monovalent electrolyte solution*

As a particular example within the general framework developed in Section 2, we consider a charged, porous medium in a bathing solution consisting of water and a dissociated monovalent strong electrolyte (e.g., NaCl). The subscripts + and − will indicate quantities relevant to the positive and negative ions, respectively.

For this system, the variational equation is :

$$
\begin{aligned}
\int_{\Omega_0} \Big\{ & [\boldsymbol{S}^e - (p+\pi)J\boldsymbol{B}] : \delta\dot{\boldsymbol{E}} + p\delta\dot{\xi} - \delta\dot{p}(J-1-\xi) + \delta\dot{\Phi}(\rho_{m_0} + \mathscr{F}C_+ - \mathscr{F}C_-) \\
& + \left[\bar{v}_+ + \frac{\partial U(\boldsymbol{A}, C_+, C_-)}{\partial C_+}\right]\delta\dot{C}_+ + \left[\bar{v}_- + \frac{\partial U(\boldsymbol{A}, C_+, C_-)}{\partial C_-}\right]\delta\dot{C}_- \\
& + \delta\dot{\mathscr{W}}\cdot(\boldsymbol{R}_{ff}\cdot\dot{\mathscr{W}} + \boldsymbol{R}_{f+}\cdot\mathscr{J}_+ + \boldsymbol{R}_{f-}\cdot\mathscr{J}_-) \\
& + \delta\mathscr{J}_+\cdot(\boldsymbol{R}_{+f}\cdot\dot{\mathscr{W}} + \boldsymbol{R}_{++}\cdot\mathscr{J}_+ + \boldsymbol{R}_{+-}\cdot\mathscr{J}_-) \\
& + \delta\mathscr{J}_-\cdot(\boldsymbol{R}_{-f}\cdot\dot{\mathscr{W}} + \boldsymbol{R}_{-+}\cdot\mathscr{J}_+ + \boldsymbol{R}_{--}\cdot\mathscr{J}_-)\Big\}\,\mathrm{d}\Omega \\
& - \int_{\Gamma_0} (\boldsymbol{f}\cdot\delta\boldsymbol{v} - p\boldsymbol{N}\cdot\delta\dot{\mathscr{W}} - v_+\boldsymbol{N}\cdot\delta\mathscr{J}_+ - v_-\boldsymbol{N}\cdot\delta\mathscr{J}_-)\,\mathrm{d}\Gamma = 0. \qquad (55)
\end{aligned}
$$

As we wish to specify the current density on the boundary, it is natural to choose $\boldsymbol{j}_{el}$ as one of the new flux variables :

$$\boldsymbol{j}_{el} = \mathscr{F}(\boldsymbol{j}_+ - \boldsymbol{j}_-). \qquad (56)$$

This electrical flux represents the flow of unbalanced solute charge. As the other chemical flux variable, we choose the balanced electrolyte flux, $\boldsymbol{j}_b$, which represents the flux of co-transporting Na$^+$ and Cl$^-$ ions. Because the matrix fixed charge density in articular cartilage is negative, we choose to associate the balanced electrolyte flux with the minority ionic species, Cl$^-$:

$$\boldsymbol{j}_b = \boldsymbol{j}_-. \qquad (57)$$

This choice is arbitrary, as we could have chosen the flux of Na$^+$ with equal success. We retain the relative fluid velocity $\overset{*}{\boldsymbol{w}}$ as the third flux variable.

To determine the appropriate thermodynamic potentials corresponding to the new flux variables, we utilize the fact that the dissipative power for the reformulated problem must be identical to that for the original problem. Specializing eqn (41) to this example and regrouping terms yields :

$$P^{\text{diss}} = \int_{\Omega_0} -\left[\textsc{grad}\, p\cdot\dot{\mathscr{W}} + \textsc{grad}(\bar{\mu}_+ + \bar{\mu}_-)\cdot\mathscr{J}_b + \textsc{grad}\left(\Phi + \frac{\bar{\mu}_+}{\mathscr{F}}\right)\cdot\mathscr{J}_{el}\right]\mathrm{d}\Omega. \qquad (58)$$

Consequently, we see that $\textsc{grad}\,\bar{\mu}_b$ and $\textsc{grad}\,\theta$ are the proper thermodynamic conjugates to $\mathscr{J}_b$ and $\mathscr{J}_{el}$, respectively, where :

Table 2. Local equations implied by the global variational equation [eqn (63)] for a porous medium infused by a binary monovalent electrolyte

Linear momentum balance	$\mathrm{DIV}\,\boldsymbol{T} = \boldsymbol{0}$ in Ω_0
Mass conservation	$J-1-\xi = 0$ in Ω_0
Charge conservation	$\rho_0 = 0$ in Ω_0
Generalized Darcy's law	$\mathrm{GRAD}\,p-\boldsymbol{R}_{ff}\cdot\dot{\mathcal{W}}-\boldsymbol{R}_{fb}\cdot\mathcal{J}_b-\boldsymbol{R}_{fe}\cdot\mathcal{J}_{el} = \boldsymbol{0}$ in Ω_0
Generalized Fick's law	$\mathrm{GRAD}\,\bar{\mu}_b-\boldsymbol{R}_{bf}\cdot\dot{\mathcal{W}}-\boldsymbol{R}_{bb}\cdot\mathcal{J}_b-\boldsymbol{R}_{be}\cdot\mathcal{J}_{el} = \boldsymbol{0}$ in Ω_0
Generalized Ohm's law	$\mathrm{GRAD}\,\theta-\boldsymbol{R}_{ef}\cdot\dot{\mathcal{W}}-\boldsymbol{R}_{eb}\cdot\mathcal{J}_b-\boldsymbol{R}_{ee}\cdot\mathcal{J}_{el} = \boldsymbol{0}$ in Ω_0
Traction boundary condition	$\boldsymbol{N}\cdot\boldsymbol{T}-\boldsymbol{f} = \boldsymbol{0}$ on Γ_{0_Γ}
Pressure boundary condition	$p-\hat{p} = 0$ on Γ_{0_p}
Chemical boundary condition	$\bar{\mu}_b+\dfrac{\partial U(\boldsymbol{A},C_b,\rho_0)}{\partial C_b}-\hat{\mu}_b = 0$ on Γ_{0_b}
Electrical boundary condition	$\theta+\dfrac{\partial U(\boldsymbol{A},C_b,\rho_0)}{\partial \rho_0}-\hat{\theta} = 0$ on Γ_{0_θ}

Note that $\hat{p}$, $\hat{\mu}_b$ and $\hat{\theta}$ are values prescribed on portions of the boundary. Because it is expressed in terms of θ, the electrical boundary condition incorporates information about both the electrical potential Φ and the electrolyte concentration in the bath.

$$\bar{\mu}_b = \bar{\mu}_+ + \bar{\mu}_-, \tag{59}$$

$$\theta = \Phi + \frac{\bar{\mu}_+}{\mathcal{F}} = \frac{\bar{\nu}_+}{\mathcal{F}}. \tag{60}$$

In order to evaluate $\bar{\mu}_+$ and π, we derive from eqns (14) and (38) the following expression for $\bar{c}_+$ in this system:

$$\bar{c}_+ = \bar{c}_b + \frac{\rho_0 - \rho_{m_0}}{\mathcal{F} J \phi^f}, \tag{61}$$

where, assuming macroscopic electroneutrality in the reference state, the net charge density per unit reference volume is:

$$\rho_0 = -\mathrm{DIV}\,\mathcal{G}_{el}. \tag{62}$$

We include ρ_0 in eqn (61) because electroneutrality (i.e., $\rho_0 = 0$) will be implicitly enforced in our formulation and should not be explicitly assumed. The gradient of the apparent pressure is retained as the conjugate to the relative fluid velocity.

Given these definitions, the variational equation for this system becomes:

$$\begin{aligned}
\int_{\Omega_0} \Bigg\{ & [\boldsymbol{S}^e - (p+\pi)J\boldsymbol{B}] : \delta\dot{\boldsymbol{E}} + p\delta\dot{\xi} - \delta\dot{p}(J-1-\xi) + \delta\dot{\Phi}\rho_0 \\
& + \left[\bar{\mu}_b + \frac{\partial U(\boldsymbol{A},C_b,\rho_0)}{\partial C_b}\right]\delta\dot{C}_b + \left[\theta + \frac{\partial U(\boldsymbol{A},C_b,\rho_0)}{\partial \rho_0}\right]\delta\dot{\rho}_0 \\
& + \delta\dot{\mathcal{W}}\cdot(\boldsymbol{R}_{ff}\cdot\dot{\mathcal{W}} + \boldsymbol{R}_{fb}\cdot\mathcal{J}_b + \boldsymbol{R}_{fe}\cdot\mathcal{J}_{el}) + \delta\mathcal{J}_b\cdot(\boldsymbol{R}_{bf}\cdot\dot{\mathcal{W}} + \boldsymbol{R}_{bb}\cdot\mathcal{J}_b + \boldsymbol{R}_{be}\cdot\mathcal{J}_{el}) \\
& + \delta\mathcal{J}_{el}\cdot(\boldsymbol{R}_{ef}\cdot\dot{\mathcal{W}} + \boldsymbol{R}_{eb}\cdot\mathcal{J}_b + \boldsymbol{R}_{ee}\cdot\mathcal{J}_{el}) \Bigg\}\,\mathrm{d}\Omega \\
& - \int_{\Gamma_0} (\boldsymbol{f}\cdot\delta\boldsymbol{v} - p\boldsymbol{N}\cdot\delta\dot{\mathcal{W}} - \mu_b\boldsymbol{N}\cdot\delta\mathcal{J}_b - \theta\boldsymbol{N}\cdot\delta\mathcal{J}_{el})\,\mathrm{d}\Gamma = 0.
\end{aligned} \tag{63}$$

Note that we still treat Φ (not θ) as an independent variable. This poses no difficulty, as θ can be evaluated as a function of Φ, C_b and ρ_0. The local equations implied by eqn (63) (Table 2) are consistent with those from the general formulation (Table 1) and specify all of the appropriate conditions for the medium. For example, the boundary condition for the chemical potential of the neutral salt implies the following at the boundary with a fully dissociated solution of salt concentration $\hat{c}_b$:

$$\exp\left[\frac{1}{RT}\frac{\partial U(\boldsymbol{A}, C_b, \rho_0)}{\partial C_b}\right]\bar{\gamma}_+\bar{\gamma}_-\bar{c}_+\bar{c}_- = \gamma_+\gamma_-\hat{c}_+\hat{c}_- = \gamma_\pm^2\hat{c}_b^2. \tag{64}$$

For a material in which the solid matrix elasticity is not affected by the interstitial solute concentrations, the argument of the exponential term goes to zero, yielding a standard equation for chemical equilibrium between phases. Likewise, the electrical boundary condition implies the following expression for the electrical potential difference across the boundary:

$$\begin{aligned}\bar{\Phi}-\hat{\Phi} &= RT\ln\frac{\bar{a}_+}{\hat{a}_+} - \frac{\partial U(\boldsymbol{A}, C_b, \rho_0)}{\partial \rho_0}\\ &= RT\ln\left[\frac{\bar{\gamma}_+}{\gamma_+}\left(-\frac{\rho_{m_0}}{2\mathscr{F}J\phi^f\hat{c}_b}+\sqrt{\left(\frac{\rho_{m_0}}{2\mathscr{F}J\phi^f\hat{c}_b}\right)^2+\frac{\gamma_+\gamma_-}{\bar{\gamma}_+\bar{\gamma}_-}}\right)\right]-\frac{\partial U(\boldsymbol{A}, C_b, \rho_0)}{\partial \rho_0}.\end{aligned} \tag{65}$$

If the solid equilibrium is independent of the interstitial composition, then eqn (65) becomes the expression for the Donnan potential difference across the boundary.

In this reformulated problem, we must specify either the balanced solute flux or the salt concentration (and therefore chemical potential) over the entire boundary, and we must specify either the electrical current density or the potential θ over the entire boundary. Thus, as intended, this reformulated problem is mathematically more convenient than the original formulation for imposing electrical boundary conditions on the porous medium. Once a given problem is solved, the individual solute fluxes can be determined using eqns (56) and (57).

3.2. *Example* 2: *Ternary solution*

We now briefly consider a ternary system involving the binary electrolyte of Example 1 plus an extra, possibly charged solute species denoted by the subscript "x". Such systems are used in the study of mechanically or electrically enhanced transport of nutrients or cytokines through the tissue (Garcia *et al.*, 1996). The procedure for deriving a consistent reformulation is directly analogous to that described in the preceding example. In this case, convenient independent fluxes are $\overset{*}{\boldsymbol{w}}$, $\boldsymbol{j}_b$, $\boldsymbol{j}_{el}$ and the flux of the additional species, $\boldsymbol{j}_x$. The balanced electrolyte flux $\boldsymbol{j}_b$ is defined as in Example 1, but the electrical current density is now defined as:

$$\boldsymbol{j}_{el} = \mathscr{F}(\boldsymbol{j}_+ - \boldsymbol{j}_- + z_x\boldsymbol{j}_x). \tag{66}$$

Note that the expression used to derive $\bar{c}_+$ changes accordingly:

$$\bar{c}_+ = \bar{c}_b - z_x\bar{c}_x + \frac{\rho_0-\rho_{m_0}}{\mathscr{F}J\phi^f}. \tag{67}$$

Once again, we specialize eqn (41) to the present example and group terms corresponding to the new set of flux variables:

$$\begin{aligned}P^{\text{diss}} = \int_{\Omega_0} -\Bigg[&\text{GRAD}\,p\cdot\dot{\mathscr{W}}+\text{GRAD}(\bar{\mu}_+ + \bar{\mu}_-)\cdot\mathscr{J}_b\\ &+\text{GRAD}\left(\Phi+\frac{\bar{\mu}_+}{\mathscr{F}}\right)\cdot\mathscr{J}_{el}+\text{GRAD}(\bar{\mu}_x - z_x\bar{\mu}_+)\cdot\mathscr{J}_x\Bigg]\mathrm{d}\Omega.\end{aligned} \tag{68}$$

Thus, p, $\bar{\mu}_b$ and θ as defined in Example 1 are still the appropriate potentials corresponding to $\dot{\mathscr{W}}$, $\mathscr{J}_b$ and $\mathscr{J}_{el}$, respectively, and $\bar{\alpha}_x$ corresponds to $\mathscr{J}_x$, where:

$$\bar{\alpha}_x = \bar{\mu}_x - z_x\bar{\mu}_+. \tag{69}$$

With simple modifications of eqn (63) to reflect the contributions of the additional species, we derive a variational equation for this ternary system. The following terms are added to eqn (63):

$$\int_{\Omega_0} \left\{ \left[\bar{\alpha}_x + \frac{\partial U(\boldsymbol{A}, C_b, \rho_0, C_x)}{\partial C_x} \right] \delta\dot{C}_x + \delta\dot{\mathscr{W}}\cdot\boldsymbol{R}_{fx}\cdot\mathscr{J}_x + \delta\mathscr{J}_b\cdot\boldsymbol{R}_{bx}\cdot\mathscr{J}_x + \delta\mathscr{J}_{el}\cdot\boldsymbol{R}_{ex}\cdot\mathscr{J}_x \right.$$
$$\left. + \delta\mathscr{J}_x\cdot(\boldsymbol{R}_{xf}\cdot\dot{\mathscr{W}} + \boldsymbol{R}_{xb}\cdot\mathscr{J}_b + \boldsymbol{R}_{xe}\cdot\mathscr{J}_{el} + \boldsymbol{R}_{xx}\cdot\mathscr{J}_x) \right\} \mathrm{d}\Omega + \int_{\Gamma_0} \alpha_x \boldsymbol{N}\cdot\delta\mathscr{J}_x\,\mathrm{d}\Gamma. \tag{70}$$

The definitions of ρ_0 and $\delta\dot{\rho}_0$ in eqn (63) must be modified to be consistent with eqn (66), and the osmotic pressure π will now include a contribution from the additional solute species. Additionally, we have allowed (via $U(\boldsymbol{A}, C_b, \rho_0, C_x)$) for the possibility that the presence of the new solute species may alter the elastic behavior of the solid matrix. As required by the specific physical problem, this approach can be extended to an arbitrary number of solute species.

4. SUMMARY

In this study, we developed a general framework for quasistatic analysis of coupled physicochemical flows in charged porous media under finite deformations. We first constructed a thermodynamic description of energy storage and transfer involving an intrinsically incompressible solid matrix, an intrinsically incompressible interstitial fluid and an arbitrary number of solute species. After introducing the phenomenological coupling laws of nonequilibrium thermodynamics, we applied the variational principle of virtual power. This produced a variational equation that implied the appropriate local governing equations for the porous media (e.g., conservation of momentum, conservation of mass, etc.).

Our description of the porous medium in terms of fluid and solute fluxes relative to a single continuum follows in the tradition of classical biophysics and nonequilibrium thermodynamics (DeGroot and Mazur, 1969; Friedman, 1986; Katchalsky and Curran, 1967), and is essentially an extension of these approaches that allows for finite deformations. With appropriate constitutive assumptions, analyses based on this formulation will be consistent with previous models that neglected chemical potential gradients (Lewis and Garner, 1972; Levenston *et al.*, 1997, 1998b) and others that neglected electrical potential gradients (Lai *et al.*, 1991; Snijders *et al.*, 1995; Simon *et al.*, 1996).

An advantage of the variational formulation we have adopted is that it allows us to change assumptions about material behavior and derive a new, fully consistent set of local governing equations for the medium. For example, a microcontinuum averaging approach could be used to generate a different relationship between the average chemical concentrations and the free energy density based on a particular microstructural model. This would alter the apparent solution behavior at the macroscopic level, resulting in a different dependence of the effective electrochemical potential [eqn (34)] on the average interstitial concentrations. Consequently, the interstitial concentrations required for equilibrium with a bathing solution would differ from the values predicted based on average concentrations. Likewise, the dependence of the osmotic pressure on the average concentrations would change [eqn (52)], and the swelling response to changes in the external bath would thus be altered.

Although predictions based on average interstitial solute concentrations are reasonable for many porous media, this is not always the case for biological tissues. For example, the osmotic behavior of articular cartilage has been shown experimentally to differ from the behavior predicted by a simple Donnan macromodel (Eisenberg and Grodzinsky, 1985; Lai *et al.*, 1991), prompting the use of empirical corrections in constitutive laws for the total stress on the porous medium. This approach is often necessary in order to accurately predict the observed mechanical behavior of microstructurally complex tissues. For full consistency, however, corresponding modifications should be made to the constitutive law for the electrochemical potential, so that any non-ideal osmotic behavior is mirrored in non-ideal electrochemical equilibrium conditions. This issue also has implications for numerical solutions of the governing equations, as changing the form of the osmotic stress without a corresponding change in the electrochemical potential will introduce asymmetries into the finite element stiffness matrix (Appendix B).

As discussed in Appendix B, the variational framework developed in this study is quite naturally implemented as a mixed finite element method. The resulting implementation is appropriate for analysis of the nonlinear, inhomogeneous, anisotropic behavior typical of biological tissues. Although motivated primarily by the study of biological tissues, this new formulation may be of general use in analyzing geometrically and materially complex problems involving charged porous media in the fields of biomechanics, membrane physics and geomechanics.

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APPENDIX A: CONSTITUTIVE RELATIONS

As mentioned in Section 2.4, the coupling tensors in the phenomenological coupling law [eqn (43)] could be derived using a microcontinuum averaging approach. Alternatively, the coupling tensors could be prescribed through macrocontinuum level constitutive relations. For example, the flux of an individual species is often modeled by (Helfferich, 1962):

$$\boldsymbol{j}_i = -\bar{c}_i \bar{\boldsymbol{D}}_i \cdot \nabla \bar{v}_i + \bar{c}_i \overset{*}{\boldsymbol{w}}, \tag{71}$$

where $\bar{\boldsymbol{D}}_i$ is the "effective" diffusivity tensor within the porous medium. This equation adds a solute convection term to the Nernst–Planck (or electrodiffusion) equation, which assumes that a concentration gradient of one species does not directly affect transport of any other species. Combining eqn (71) with the first line of eqn (43) yields:

$$\boldsymbol{j}_i = \bar{c}_i \left[\boldsymbol{l}_{ff} \cdot \nabla p + (\boldsymbol{l}_{fi} - \bar{\boldsymbol{D}}_i) \cdot \nabla \bar{v}_i + \sum_{k,k \neq i} \boldsymbol{l}_{fk} \cdot \nabla \bar{v}_k \right]. \tag{72}$$

Comparison of this equation with the remainder of eqn (43) leads to the following expressions:

$$\boldsymbol{l}_{if} = \bar{c}_i \boldsymbol{l}_{ff} \tag{73}$$

$$\boldsymbol{l}_{ii} = \bar{c}_i^2 \boldsymbol{l}_{ff} - \bar{c}_i \bar{\boldsymbol{D}}_i \tag{74}$$

$$\boldsymbol{l}_{ik} = \bar{c}_i \boldsymbol{l}_{fk}, \quad k \neq i. \tag{75}$$

Because $\boldsymbol{l}_{ik} = \boldsymbol{l}_{ki}$ due to Onsager reciprocity, we have reduced to $n+1$ the number of independent tensors in eqn (43) for a medium containing n solute species. The coupling tensors for a system reformulated as in Section 3 can be derived as linear combinations of these tensors.

As an example, a microstructural model such as the unit cell model of Happel (1959) could be used to define the deformation dependence of $\boldsymbol{l}_{ff}$, sometimes described as the "short circuit" permeability because it describes fluid flow in the absence of any solvent electrochemical potential gradients. The apparent diffusivity tensors could be described using the isotropic tortuosity factor of Mackie and Meares (1955), which is a simple model for changes in the diffusion path with matrix deformation:

$$\bar{\boldsymbol{D}}_i = \left(\frac{\phi^f}{2 - \phi^f} \right)^2 D_i \boldsymbol{I}, \tag{76}$$

where D_i is the diffusivity of species i in free solution and could generally depend on the concentration. Because ϕ^f changes with deformation [eqn (20)], the $\bar{\boldsymbol{D}}_i$ are deformation dependent.

The final constitutive law to be specified is the hyperelastic stored energy density $U(A, C_1, \ldots, C_n)$ representing the Helmholtz energy density associated with macroscopic deformation of the solid matrix for a given physicochemical state. In practice, it may be quite difficult to separate the deformation and osmotic effects. For example, the "solid" properties of articular cartilage are usually determined via mechanical testing methods that allow fluid and solute flow across sample boundaries. Thus, the equilibrium (or "drained") stress vs deformation behavior can be determined under conditions where the apparent pressure inside the tissue is identical to that in the bath. Defining the bath pressure as zero (or reference), the total first Piola–Kirchhoff stress at equilibrium is then:

$$\boldsymbol{T}_{eq} = \boldsymbol{T}^e - \pi J \boldsymbol{F}^{-1}. \tag{77}$$

Extraction of the elastic stress from the measured equilibrium stress requires the evaluation of π, which depends on the assumptions used to define the Helmholtz free energy densities for the solutes [eqn (33)]. Alternatively, one could assess the interstitial osmotic pressure π as a function of external osmotic pressure in separate "confined" experiments that prevent bulk expansion while allowing fluid and solute flow. Any difference between π and the "ideal" osmotic pressure reflects non-ideal behavior of the interstitial solution and could be accounted for in the solute free energy densities to derive fully consistent local governing equations.

APPENDIX B: FINITE ELEMENT IMPLEMENTATION

The theoretical framework developed in Section 2 lends itself well to numerical implementation as a mixed finite element method. Finite element matrix equations for a total Lagrangian implementation are derived from the variational formulation in the usual manner (Hughes, 1987). We approximate the reference domain Ω_0 as the union of n_{el} non-intersecting elements Ω_0^e, and spatially discretize the primary variables and their real and virtual velocities. After selecting an approximate solution space for each independent variable field, we construct discretized approximations to the variables:

$$\begin{gathered}
\boldsymbol{u}^h = \mathbf{N}^{u'}\tilde{u} \quad \boldsymbol{v}^h = \mathbf{N}^{u'}\tilde{v} \quad \delta\boldsymbol{v}^h = \mathbf{N}^{u'}\delta\tilde{v} \\
\mathcal{W}^h = \mathbf{N}^{w'}\tilde{\mathcal{W}} \quad \dot{\mathcal{W}}^h = \mathbf{N}^{w'}\tilde{\dot{\mathcal{W}}} \quad \delta\dot{\mathcal{W}}^h = \mathbf{N}^{w'}\delta\tilde{\dot{\mathcal{W}}} \\
\vdots \quad \vdots \quad \vdots \\
\Phi^h = \mathbf{N}^{\Phi'}\tilde{\Phi} \quad \dot{\Phi}^h = \mathbf{N}^{\Phi'}\tilde{\dot{\Phi}} \quad \delta\dot{\Phi}^h = \mathbf{N}^{\Phi'}\delta\tilde{\dot{\Phi}}
\end{gathered} \tag{78}$$

where $()^h$ indicates a discretized approximation to the corresponding variable, $(\tilde{\ })$ indicates a vector of nodal values of $\mathbf{N}^u$, $\mathbf{N}^w$, $\mathbf{N}^\Phi$, etc. are the global shape functions describing the approximate solution spaces for the corresponding variables. As the solid boundaries define the continuum, the nodal coordinates should be isoparametric with the displacement coordinates:

$$X^h = \mathbf{N}^{u'}\tilde{X}. \tag{79}$$

Introduction of the discretizations into eqn (48) produces a semi-discretized nonlinear system of equations that must be solved via an iterative method (e.g., modified Newton–Raphson). Linearization, in combination with a time-stepping scheme, produces a fully discretized, linear matrix equation for each iteration of a given loading increment. To demonstrate the general matrix structure and degree of coupling between variables, we present the global form of the matrix equation appropriate for backwards Euler time stepping for the ternary system of Section 3.2:

$$\begin{bmatrix}
\Delta t\mathbf{K}^{uu} & \mathbf{0} & \mathbf{0} & \Delta t\mathbf{K}^{us} & \Delta t\mathbf{K}^{ux} & \Delta t\mathbf{K}^{up} & \mathbf{0} \\
\mathbf{0} & \mathbf{C}^{ff} & \mathbf{C}^{fe} & \mathbf{C}^{fb} & \mathbf{C}^{fx} & \Delta t\mathbf{K}^{fp} & \mathbf{0} \\
\mathbf{0} & \mathbf{C}^{fe'} & \Delta t\mathbf{K}^{ee}+\mathbf{C}^{ee} & \Delta t\mathbf{K}^{eb}+\mathbf{C}^{eb} & \Delta t\mathbf{K}^{ex}+\mathbf{C}^{ex} & \mathbf{0} & \Delta t\mathbf{K}^{e\Phi} \\
\Delta t\mathbf{K}^{bu'} & \mathbf{C}^{fb'} & \Delta t\mathbf{K}^{eb'}+\mathbf{C}^{eb'} & \Delta t\mathbf{K}^{bb}+\mathbf{C}^{bb} & \Delta t\mathbf{K}^{bx}+\mathbf{C}^{bx} & \mathbf{0} & \mathbf{0} \\
\Delta t\mathbf{K}^{ux'} & \mathbf{C}^{fx'} & \Delta t\mathbf{K}^{ex'}+\mathbf{C}^{ex'} & \Delta t\mathbf{K}^{bx'}+\mathbf{C}^{bx'} & \Delta t\mathbf{K}^{xx}+\mathbf{C}^{xx} & \mathbf{0} & \mathbf{0} \\
\Delta t\mathbf{K}^{up'} & \Delta t\mathbf{K}^{fp'} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\
\mathbf{0} & \mathbf{0} & \Delta t\mathbf{K}^{e\Phi'} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0}
\end{bmatrix}^{(n)}
\begin{Bmatrix}
\Delta\tilde{v} \\ \Delta\tilde{\dot{W}} \\ \Delta\tilde{\mathscr{J}}_{el} \\ \Delta\tilde{\mathscr{J}}_b \\ \Delta\tilde{\mathscr{J}}_x \\ \Delta\tilde{p} \\ \Delta\tilde{\dot{\Phi}}
\end{Bmatrix}^{(n)}
= -\begin{Bmatrix}
\mathbf{R}^u \\ \mathbf{R}^w \\ \mathbf{R}^{el} \\ \mathbf{R}^b \\ \mathbf{R}^x \\ \mathbf{R}^p \\ \mathbf{R}^\Phi
\end{Bmatrix}^{(n)} \tag{80}$$

where n is the present iteration and $\Delta(\tilde{\ })$ indicates an iterative update to the corresponding vector of nodal variables. The stiffness matrices $\mathbf{K}^{ij}$ are derived from the internal energy expression, the damping matrices $\mathbf{C}^{ij}$ are derived from the dissipative power expression, and the force vectors $\mathbf{R}^j$ are derived from the external power expression. The iterative updates to the primary variables are given by:

$$\Delta\tilde{u}^{(n)} = \Delta t\Delta\tilde{v}^{(n)}, \quad \Delta\tilde{\mathcal{W}} = \Delta t\Delta\tilde{\dot{\mathcal{W}}}^{(n)}, \quad \text{etc.} \tag{81}$$

Note that the system matrix produced with this approach is symmetric and indefinite.

As with any mixed method, care must be taken to choose element configurations that are numerically well behaved. In general, the interpolation of p should be of lower order than those if $\boldsymbol{u}$ and $\mathcal{W}$, and the interpolation of θ should be of lower order than that of $\mathscr{G}_{el}$. Because the incompressibility constraint acts on two vector fields ($\boldsymbol{u}$ and $\mathcal{W}$) while the electroneutrality constraint acts on only one vector field ($\mathscr{G}_{el}$), an interpolation scheme that satisfies the inf-sup (or Babuška–Brezzi) condition (Brezzi and Fortin, 1991), for one constraint may not be suitable for the other.

Additionally, the system matrices for multidimensional problems will be quite large. For example, a simple two-dimensional element with bilinear vector interpolations and constant Lagrange multipliers will have 42 degrees-of-freedom per element, and a 10×10 element mesh will have 1410 degrees-of-freedom. If the solution of large, multidimensional problems is necessary, efficient iterative solution methods for the indefinite linearized matrix equation may be required.